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Limitations of the Pour Point Measurement and the Influence of the Oil Composition on Its Detection Using Principal Component Analysis

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ABSTRACT: A method for maximum and minimum pour point determination in crude oil was applied, and the chemical composition of 80 samples, American Petroleum Institute (API) gravity, total acid number (TAN), density, kinematic viscosity, and sulfur, asphaltene, and wax contents were analyzed in association with chemometric methods. The results of the 80 analyzed samples showed maximum pour point temperatures from 9 to −36 °C and minimum pour point temperatures from 12 to −36 °C. Heavy oils with asphaltenic chemical composition showed more positive values of pour point (5−8 °C) and showed no significant difference between the maximum and minimum pour points considering the repeatability of the method (3 °C for maximum and 6 °C for minimum). However, the oils with chemical composition with higher wax content and higher API gravity showed lower pour point values from −24 to −6 °C (maximum) and from −30 to −18 °C (minimum), respectively. The principal component analysis (PCA) explained 92% of data variability, showing that the differences among the properties of the samples allowed for their separation by groups and some properties are closely correlated to the pour point.

1. INTRODUCTION

Crude oils are a naturally occurring complex mixture that consists of hydrocarbons, compounds of sulfur, nitrogen, and oxygen, organometallic compounds, inorganic sediments, and water.[1] The hydrocarbons present in crude oils show very distinctive physical properties if compared one to another, which are reflected on the chemical properties of these oils. These properties can vary according to the type of hydrocarbon present in petroleum that can be paraffinic, naphthenic, and aromatic. Its physical and thermodynamic properties, as well as its behavior, depend mainly upon its components, their relative amounts, and the thermodynamic conditions in which oil is found.[2,3] Hydrocarbons can be heavy, medium, or light, according to the size of their molecules. When the mixture contains a higher percentage of small or light molecules, its physical state is gaseous. When the mixture contains bigger molecules, its physical state is liquid under normal temperature and pressure conditions.[1−4]

Characterizing crude oils by measuring their physicochemical properties is essential for determining their thermodynamic behavior. It is also of high importance for oil production operations, from estimating oil existence to production projects for the transportation, refining, and distribution of oil products.[5]

An important physical property of crude oils is the pour point. This property corresponds to the lowest temperature at which oil does not flow under gravitational action, in which rheological properties of crude oil change drastically and it begins to behave as a semi-solid substance. This behavior change is associated with an increase in the formation of wax crystalline structures and an increase in oil viscosity during the cooling process, hindering the movement on the oil surface in test conditions.[6,7]

Understanding pour point in crude oils is important because it defines pipeline transfer conditions, allows for calculating dimensioning and pumping, and allows for preventive actions and process improvement, which facilitates oil flowing and reduces the incidence of incrustation because of wax and asphaltene precipitation.[3]

The pour point is imprecise, presenting low repeatability and low reproducibility. Because of the inexistence of a more significant and applicable test for petroleum and fuel oil, the pour point is kept as a useful property for indicating the product crystallization characteristics. Oils of high pour point, produced from paraffinic petroleum, need to be preheated and transported in pipelines coated with steam coils with the purpose of keeping their temperature above their pour point.[8]

The study of the pour point behavior during the production process of different oil types and its correlation with other

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characterization properties is scarce in the literature. In the case of new oil fields, a fast and efficient evaluation of the pour point of the oil allows for subsidies to the commerciality declaration of the producing field with the National Petroleum Agency (ANP).[9] Because of the fastness that the new production systems can start up the operations, it is also important to anticipate some information for the refining area, as the characteristics of the oil that is going to be produced and its blends, its classification, and identification about its origin. Therefore, the use of chemometric tools is of fundamental importance to find the correlations among the multiple physicochemical properties, including the pour point, giving fast results to allow for adjusting the operational conditions, to improve the oil flow and reduce the possibilities of wax and asphaltene precipitation, which causes several problems and can lead to the process interruption.

In this sense, the importance of understanding the pour point in oil processing and its correlation with the monitored characterization properties, American Petroleum Institute (API) gravity, total acid number (TAN), density, kinematic viscosity, and sulfur, asphaltene and wax contents, allows for the knowledge of the oil behavior when submitted to temperature variation in the primary processing and predicts the formation of deposits in the pipelines during the oil transportation and pumping.[4−8] In this aspect, the methods of multivariate statistical analysis have been successfully used to correlate, monitor, and evaluate the oil field production.[10−12] The principal component analysis (PCA) is highlighted as a powerful tool to correlate different oils similarity based on their physicochemical properties monitored during the crude oil production process.[12,13] In general, it is used for reducing the data dimensionality, detecting the number of components, visualizing the outliers, and resolving sets of data into orthogonal components, whose linear combinations approximate the original data to any desired degree of accuracy.[10,12−16]

For the great majority of Brazilian oils produced nowadays, the pour points have low-temperature values, which do not compromise the activities of production and refining. However, in a short time, most of the production will come from the pre-salt fields that are showing high-molecular-weight paraffin levels, which can have pour points altered and cause many problems in processing the oil along the production chain. In this paper, we applied a multivariate statistic technique to study the relationship of the pour point of crude oils from pre-salt and post-salt reservoirs with some intrinsic properties of crude oils.

2. EXPERIMENTAL SECTION

2.1. Treatment and Characterization of Crude Oil Samples. In this study, 80 crude oil samples were selected from production fields located in the sedimentary basin of the Brazilian coast, with three of them offshore, fields "B", "C", and "D", and one onshore, field "A". The oils derive from two reservoirs, designated as R1 (pre-salt) and R2 (post-salt) (Table 1). It is important to emphasize that, in the same field, there can be different reservoirs of petroleum with variable chemical composition and oil quantity, for example, reservoirs of post-salt and pre-salt with depth up to 4000 and 6000 m, respectively.[17] The oil samples were collected from ducts in 2 L flasks and transported to the laboratory, where they were processed within 1 h of arrival. To maintain the reproducibility of the analysis results of each collected sample, ASTM D5854[18] was followed for all of the procedures using one aliquot of the collected crude oil. During the oil treatment process, the free water (non-emulsified water) was first separated by decanting it for 1 h. After the free water separation, the water content analysis[19] was determined in the water-in-oil emulsions. Samples with a water content in excess of 2% (v/v) were dehydrated with the addition of 200 μL of the concentrated commercial demulsifier at 60 °C and centrifuged at 1600 rpm for 15 min.[17,20] These oils were called "dehydrated oil". After demulsification, the water content was again determined to verify if the water content was lower than 0.5% (v/v). Then, the pour point and other characterization properties of dehydrated crude oil samples were determined (Tables 2 and 3) according to the standard ASTM methods.

Table 1. Codes Used for the Respective Samples of Each Field and Reservoir

field	number of samples	reservoirs and fields
A	20	R2A
B	20	R1B and R2B
C	20	R1C and R2C
D	20	R2D

Table 2. Methods and Range of Physicochemical Properties of the Dehydrated Crude Oils Samples Used in This Study

physicochemical properties	results in the range	method
water content (%, v/v)	0.1−0.3	ASTM D4377[19]
API gravity at 60 °F (deg)	13.3−29.3	ASTM D1250[21]
density at 20 °C (g cm^{-3})	0.8800−0.9710	ISO 12185[22]
TAN (mg of KOH g^{-1})	0.1239−3.6321	ASTM D664[23]
kinematic viscosity at 40 °C (cSt)	8.534−850.5	ASTM D7042[24]
total sulfur content (%, w/w)	0.10−0.70	ASTM D4294[25]
asphaltene content (wt %)	0.20−16.0	IP-143[26]
wax content (wt %)	0.15−4.0	UOP 46-85[27,28]
maximum pour point (°C)	from −36 to 9	ASTM D5853[29]
minimum pour point (°C)	from −36 to 12	ASTM D5853[29]

The physicochemical properties of the dehydrated oils were also determined according to standard methods, and the ranges of the results are represented in Table 2.

2.2. Experimental Techniques for the Crude Oil Characterization. *2.2.1. Pour Point Determination.* The manual method ASTM D5853[29] is specific for measuring crude oils by determining maximum (upper) and minimum (lower) pour points. After preliminary heating, the oil samples are cooled and examined at intervals of 3 °C for checking the flow characteristics. Therefore, the lowest temperature at which movement of the sample is observed is reported as its pour point. The maximum and minimum pour point temperatures provide a temperature window, where a crude oil, depending upon its thermal history, might appear in liquid and solid states. The accuracy for pour point determination of this method follows the repeatability criteria of 3 °C for the maximum pour point and 6 °C for the minimum pour point, with 95% confidence of result acceptability.

To determine the maximum pour point, the sample was kept resting in the test jar for 24 h at room temperature to reach the equilibrium between the dissolved wax and the crystallized wax, to enhance gelation of wax crystals and solidification. Before starting the test, the resting state must be broken with a gentle stirring of the sample. The minimum pour point was measured after submitting the sample to a 105 °C heating in a pressure vessel for 30 min, to delay gelation of wax crystals and solidification.

The differential treatment under which the sample was submitted for determining the maximum pour point leads to an increase in the wax gelation and crystallization, favoring a faster solidification of the sample. On the other hand, the different treatment performed to determine the minimum pour point allows for the delay of wax crystallization, which results in slower solidification of the sample.

2.2.2. API Gravity. API gravity of the samples was determined according to ISO 12185[22] and ASTM D1250.[21] The crude oil samples

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Table 3. Physicochemical Properties Results: Average and Standard Deviation (in Parentheses)

properties	R2A	R1B	R2B	R1C	R2C	R2D
API gravity at 60 °F	13.7	28.5	19.2	29.2	17.4	28.9
	(0.23)	(0.68)	(0.10)	(0.12)	(0.27)	(0.41)
density at 20 °C (g cm^{-3})	0.9705	0.8808	0.9349	0.8770	0.9475	0.8785
	(0.0039)	(0.0043)	(0.0006)	(0.0004)	(0.0008)	(0.0022)
TAN (mg of KOH g^{-1})	0.91	0.28	1.42	0.28	3.24	0.30
	(0.015)	(0.012)	(0.031)	(0.015)	(0.114)	(0.010)
kinematic viscosity at 40 °C (cSt)	5526	29.71	452.7	29.63	621	28.46
	(159)	(0.51)	(8.5)	(0.52)	(7.3)	(1.12)
total sulfur content (%, w/w)	0.659	0.114	0.104	0.110	0.516	0.291
	(0.033)	(0.005)	(0.029)	(0.009)	(0.012)	(0.010)
asphaltene content (wt %)	12.8	1.02	1.03	0.15	0.75	0.25
	(2.08)	(0.02)	(0.03)	(0.05)	(0.18)	(0.04)
wax content (wt %)	0.2	2.3	2.3	2.2	0.3	3.5
	(0.02)	(0.12)	(0.15)	(0.13)	(0.03)	(0.39)
maximum pour point (°C)	6	−9	−30	−6	−18	−15
	(1)	(3)	(2)	(4)	(2)	(7)
minimum pour point (°C)	6	−21	−27	−18	−21	−30
	(2)	(2)	(5)	(3)	(2)	(5)

used in this study were classified as medium and heavy, and because of this, the density was measured at 50 °C and then converted to its equivalent value at 20 °C for calculating the API gravity.

2.2.3. Water Content. The water content was determined by potentiometric Karl Fischer (KF) titration, in accordance with the ASTM D4377 standard method.[19] The solvent used during the analysis was a mixture of dry methanol and 20% chloroform (v/v). For standardization of the KF reagent, distilled water was solubilized into the solvents. A Metrohm KF titrator (model 836 Titrando) equipped with a double-platinum electrode was employed during the water content determination tests.

2.2.4. Density at 20 °C. The density was determined in compliance with ISO 12185-9632[22] by injecting a sample into the digital automatic densimeter analyzer model DMA 5000 Anton Paar, a digital analyzer consisting of a U-shaped oscillating sample tube and a system for electronic excitation, frequency counting, and display.

2.2.5. TAN. The TAN was determined according to ASTM D664[23] by potentiometric titration of the crude oil with alcoholic potassium hydroxide (KOH) solution. Prior to each titration, crude oil samples were dissolved in a 50% (v/v) toluene and isopropanol solution. The same automatic titration used for KF analysis Metrohm 836 titration was employed for the acid number determination. However, this titration was equipped with a combination electrode suitable for non-aqueous titrations.

2.2.6. Kinematic Viscosity. Above the wax appearance temperature (WAT), the rheological behavior of crude oils is generally Newtonian. When the temperature approaches the pour point, a sharp increase in viscosity may be seen in offshore pipelines transporting waxy crude oils. The non-Newtonian behavior can give rise to very high pressure drops and cause problems because the oil may gel completely and develop a significant gel strength.[30]

The kinematic viscosity was determined according to ASTM D7042.[24] This was measured at 50 and 60 °C and then estimated at 40 °C by regression, as contained in the Petrobras technical bulletin.[31] The kinematic viscosity was determined by injecting a sample into the digital automatic viscosimeter analyzer Stabinger SVM 3000 Anton Paar.

2.2.7. Total Sulfur Content. The total sulfur content was determined according to ASTM D4294[25] by energy-dispersive X-ray fluorescence spectrometry using the automatic analyzer HORIBA, model SFLA-2800. Three calibration curves were built [0.005−0.100% (w/w), 0.05−1.00% (w/w), and 0.3−4.0% (w/w)], using 10 sulfur patterns in mineral oil marks INSTRU-MED, which were automatically selected by the equipment in agreement with the sample to be analyzed. The calibration curve verification was accomplished through the analysis of a diesel reference sample, with seven repetitions.

2.2.8. Asphaltene Content. Asphaltenes may associate to form colloidal-sized particles that strongly influence the viscosity of the medium crude oil and affect the crystallization of the wax and its pour point.[32]

The asphaltene content was determinated by extracting and quantifying each atmospheric residue sample according to the IP-143 method.[26] This method consisted of stirring 10 g of each residue in 400 mL of *n*-heptane [99.5% (w/w) purity] with a magnetic stirrer for 2 h. The mixture was left resting for 60 h. After that, the material was filtered using a 20 cm diameter quantitative paper filter. The material retained on the filter was washed with *n*-heptane until the solvent filtered presented its original color. Then, the filter paper was closed as a cylindrical cartridge and moved into an Soxhelet extractor. In the extractor, it was added *n*-heptane for a hot extraction, to guarantee the removal of all soluble materials in this solvent. When the solvent was showing no color, it was changed into toluene [99.5% (w/w) purity]. The extraction was considered over when this solvent did not show a dark color in the extractor anymore. The baloon containing toluene with the dissolved asphaltenes was submitted to a rotaevaporator for vaporization under reduced pressure and a maximum temperature of 50 °C. The baloon containing asphaltenes with no toluene was weighed, and the extracted mass is expressed as the asphaltene content measured (wt %).

2.2.9. Wax Content. The wax present in the crude oil is responsible for the high pour point and complex rheology (non-Newtonian flow) of the crude oil.[33]

The wax content was determined by the modified UOP method 46-85[27,28] that is based on the wax precipitation by acetone. Crude oil was dissolved in *n*-pentane and stirred for 30 min. Acetone (acetone/*n*-pentane ratio of 3:1) was added to the mixture and cooled to −20 °C for 24 h. The solid phase present in the oil was separated by filtration in a Buchner funnel using a glass microfiber Whatman filter number 934. The solid phase was redissolved in *n*-hexane to remove its asphaltenes. After solvent removal, the final product was weighed and the wax content was evaluated (wt %).

2.2.10. PCA. PCA is a statistical method used to reduce the dimension of a data set (matrix **X**) while maintaining most of its variance.[10,11] The original variables are linearly transformed into new variables called principal components (PCs). The PC is ordered to retain most of the data variance. Thus, the first PC contains most of the variance, etc. In this decomposition, two small matrices are formed, loading (**P**) and scores (**T**). These matrices, **P** and **T**, capture the essential data patterns of **X**, and the non-essential part is the residual matrix (**E**).

$$\mathbf{X} = \mathbf{T}\mathbf{P}^T + \mathbf{E} \quad (1)$$

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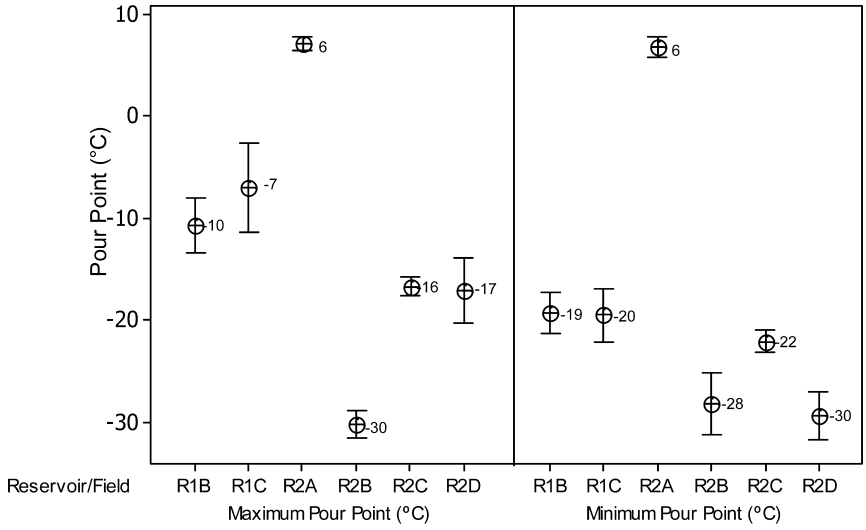

Figure 1. Mean variance graph of the maximum and minimum pour point results, separated by reservoir and field with a confidence interval of 95%.

The loading provides information with respect to the variables used in the statistical analysis, while scores provides information about the samples, thus allowing for the visualization of the outliers and clusters of samples by their similarities.[10] In this paper, PCA was applied to derive the first two main components from the properties of characterization and to examine the possible grouping of samples. The matrix **X** was pre-processed by autoscaling to equal the variable magnitudes. The Minitab statistical software was used for data analysis (release 14.13, Minitab, Inc., State College, PA).[34]

3. RESULTS AND DISCUSSION

3.1. Crude Oil Properties. Analyzes were carried out to characterize the 80 dehydrated crude oils studied in this work. The water content, API gravity, density at 20 °C, TAN, kinematic viscosity, total sulfur content, asphaltene content, wax content, and pour point temperatures of each crude oil sample were measured as described above, and the results are reported in Table 3. The results show that the dehydration of the 80 selected samples was performed with efficiency because the final water content was below 0.3% (v/v). The oil characterization shows that the crude oils studied here are classified as medium and heavy crude oils.

3.2. Results of Pour Point Determination. When the thermal history is known, the maximum pour point shows a tendency to present higher values than the minimum pour point (Table 3). In practice, it is most usual to consider the maximum pour point for keeping control of the oil flow process. The results of the maximum pour point for the 80 analyzed samples were obtained with accuracy of the ASTM 5853 method, with 95% confidence of result acceptability. Table 3 showed that the pour point variability presented a negative to positive average (from −30 to 6 °C). The post-salt oil reservoir R2A presented positive pour points, which are undesirable in the oil chain. The pour point behavior of these samples can be explained by the fact that these are heavy oils with high viscosity values and high asphaltene and sulfur contents in their chemical composition. The oils in the pre-salt (R1B and R1C) reservoirs presented pour point values above the oils from the post-salt (R2C, R2B, and R2D), and this behavior can be explained by the fact that these oils presented intermediate chemical composition with higher API gravity, low viscosity and TAN, and high wax content. The R2B oils (heavy oils) presented an aromatic chemical composition with a moderate acidity content and showed lower pour points when compared to the R2C and R2D oils. The R2C samples were characterized as heavy oils, naphthenic, and high values of TAN. The R2D samples presented pour point values next to R1B and R1C samples and high API gravity, besides coming from different reservoirs.

3.3. Mean Results of the Maximum and Minimum Pour Points for the Selected Samples within Each Reservoir and Field. The results represented on graphs (Figure 1) showed that the pour point mean variability measurement presented negative to positive values from −30.0 to 6.0 °C for the maximum pour point and from −30.0 to 6.0 °C for the minimum pour point. The field "A" (on-shore, reservoir R2) presented the highest pour point values with variation of 5.0−8.0 °C in maximum and minimum pour points, respectively. This variation is in agreement with the method repeatability criteria of 3 and 6 °C in maximum and minimum pour points, with a confidence interval of 95%, respectively, while the samples of other fields showed pour point variations outside the method repeatability criteria.

The offshore fields "B" and "C" presented samples from R1 and R2 reservoirs. The samples from the R1 reservoir showed maximum and minimum pour points higher than samples from the R2 reservoir. It was expected that the R1 reservoir would present the highest values for the minimum and maximum pour points because of its higher wax content if compared to the R2 reservoir, but the R2A samples were the samples that presented the highest pour point values. It can be explained by the fact that, although these samples presented the lowest wax content, they are the samples with the highest viscosities levels, which led to the highest pour points.

It is also important to highlight that the difference between maximum and minimum pour points is based on the previous treatment that the samples were submitted to manipulate the wax equilibrium in the solution. Therefore, when the wax content was low (i.e., R2A samples), there was no significant difference between the maximum and minimum pour points, with the viscosity being the main factor to explain the pour point values. In situations where maximum and minimum pour points are positive and similar, there is a flow problem because it is not possible to cause changes on the pour point when the oil is previously treated with heat and high pressure.

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3.4. PCA. After characterization of the physicochemical properties of the crude oil, the PCA was applied to the data to verify the similarity among the physicochemical properties of the analyzed oils and the similarity among the samples, evaluate tendencies, and verify possible outliers. Just from analysis of the pour point results (Table 3), it is not possible to classify and identify these profiles; therefore, the PCA provides additional information to reach the objective in question.

The scores plot from PCA (Figure 2) shows a plot of the samples in the new coordinate system, called PCs. The samples

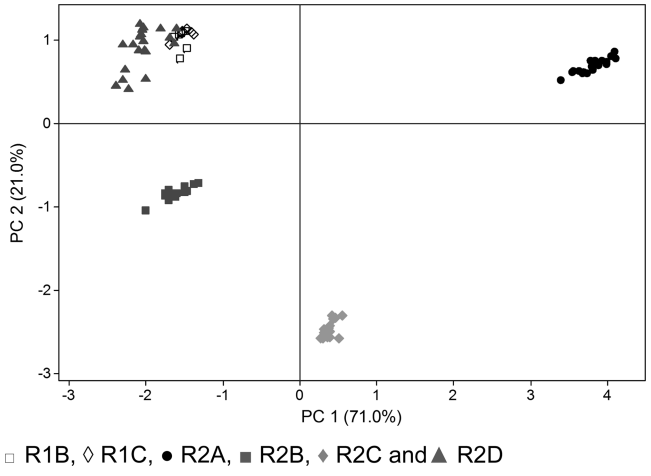

Figure 2. Scores plot (PC1 versus PC2) of the analyzed samples by the reservoirs and fields with 92.0% of the total variance explained by two first PCs.

were closely grouped into four classes. Oils of post-salt (R2A, R2B, and R2C) are clearly separated, while R2D shows similar features to those of the pre-salt oils (R1B and R1C), forming a group of these samples. This separation was possible because of the high correlation among the physicochemical properties of the analyzed oils.

In the loading plot (Figure 3), the original variables are represented as vectors in the new PC system. The larger cosine of the angle between the variables will be higher than the correlation between them. The results from the loadings plot PCA suggested the correlation levels among these properties because of the angles among the vectors. To check the studied sample profile, the properties of density, kinematic viscosity,

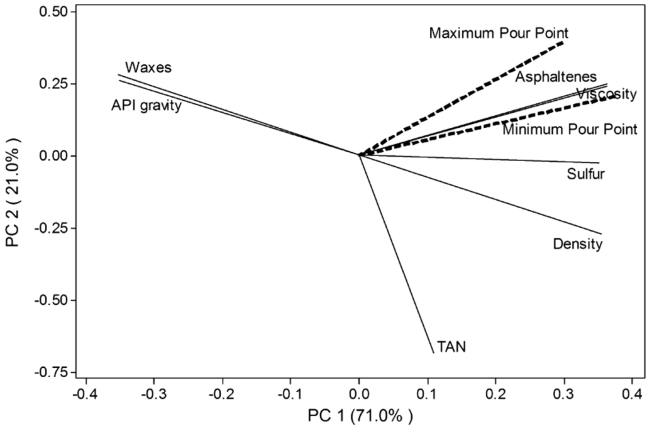

Figure 3. Loadings plot (PC1 versus PC2) of the characterization properties of the analyzed samples.

TAN, sulfur content, asphaltene content, and pour point were selected to the correlation study and the two first components (PC1 versus PC2) were enough to correlate the data because it contains 92.0% of the total variability in the data set.

The R2A samples were separated because of the high loading of the asphaltenes, kinematic viscosity, and minimum and maximum pour points, which enabled its separation from the other groups. This behavior can be explained by the positive values of the pour point presented by the field A (Figure 1). These results show that field A presented a heavy oil behavior because of not only their low API gravity but also their high correlation with asphaltenes and viscosity as well. The R2B samples showed intermediate properties among API gravity, wax content, and TAN properties. The R2C samples were grouped according to the TAN property and showed the highest values of acidity if compared to the other samples.

Although the R1B, R1C, and R2D samples were obtained from different reservoirs/fields, all of them were grouped in the same group according to the high correlation with API gravity and wax content (Figures 2 and 3).

4. CONCLUSION

The study presented results variability from positive to negative pour point values, which allowed for an assessment of the maximum and minimum pour points of the analyzed samples. It was found that the heavy oils had higher pour point values (more positive), with no difference between the minimum and maximum pour points, and the results obtained were within the range of the method repeatability. This behavior can be explained by the chemical composition of the analyzed oils.

The limitations associated with the pour point measurements are based on the fact that sometimes the expected behavior is not observed. For example, it is expected that oils with a higher wax content present a higher pour point, but it is observed that this expected behavior can vary in function of the multiple physicochemical properties of the oil composition. Thus, the evaluation of multivariate physicochemical properties of oils can provide more information more quickly than the observation of these variables individually.

The PCA showed a high correlation among kinematic viscosity, asphaltene content, and pour point. However, this behavior was not observed in high API gravity oils with low viscosity and high wax content, which presented lower pour point values (more negative). Thus, the PCA presented to be an efficient tool to analyze the physicochemical properties and their correlations of petroleum samples from different reservoirs/fields.

It can also be concluded that the analyzed oils presented a wide range of composition and properties. These differences could be found inside the same production field but with different reservoirs with different depths.

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Notes

The authors declare no competing financial interest.

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